$CH_4 < NH_3 < H_2O < HF$

⟶ Electronegativity ↑es.

⟶ Acid strength ↑es.

Common Ion Effect in the Ionization Of Acids and Bases.

The shift in the Eqlbm on adding a substance that provides more of an ionic species already present in the dissociation Eqlbm. (It is in accordance with Le Chatelier's principle)

So, If a salt of weak Acid is added to a solution of the acid itself, dissociation of the acid ↓es further.

$CH_3COONa \longrightarrow CH_3Na^+ + CH_3COO^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \longrightarrow (1)$

the addition of CH_3COO^- ions supplied by CH_3COONa pushes the Eqlbm to left (eq^n (1)) as a result the dissociation of acetic acid is suppressed.

Hardy, $NH_4OH \rightleftharpoons NH_4^+ + OH^- \longrightarrow (2)$

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

Mixture of Weak Acids and Salts:-

Suppose a weak monobasic acid HA

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = [H^+][A^-] / [HA]$$

$$[H^+] = K_a [HA]/[A^-] \longrightarrow (1)$$

Now if there is a mixture of weak Acid and its strong salt NaA. Let $C_1 = [HA]$ and C_2 [NaA]

We know HA is weak Acid, so Ka is also very small which is further supressed by common ion of NaA, ∴ in the mixture ⇒

$$[A^-] = C_2$$

where as $[HA] = C_1$.

So the equation (1) becomes

$$[H^+] = K_a \frac{C_1}{C_2}$$

or In general $[H^+] = K_a C_1 / C_2$

$$= K_a \frac{[Acid]}{[salt]}.$$

So, as the ratio of acid / salt ↓es., the $[H^+]$ ↓es.

Ques What will be the hydrogen ion conc. of a soln obtained by mixing 500 mL of 0.20M. Acetic Acid and 500 mL of 0.30M Sodium acetate? (K_a (ACH) = 1.75×10^{-5})

Total vol. of soln = 1000 mL

Soln ∴ [AcH] in mixture = $\frac{0.20}{1000} \times 500$ mL = 0.10 M.

[NaA] " = $\frac{0.30}{1000} \times 500$ mL = 0.15 M.

$$[H^+] = K_a \frac{[\text{acid}]}{\text{Salt}}$$

$$= \frac{1.75 \times 10^{-5} \times 0.10}{0.15} = 1.17 \times 10^{-5} \text{ mol/dm}^3.$$

Ques - Calculate the pH of a 0.10M of ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10 M HCl. The dissociation constant of NH_3 $K_b = 1.77 \times 10^{-5}$.

Ans

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.77 \times 10^{-5}$$

So $[NH_4^+] = [OH^-] = x$ (Before Neutralization)

$[NH_3] = 0.10 - x \simeq 0.10$

$\therefore 1.77 \times 10^{-5} = \frac{(x)(x)}{0.10}$

$\Rightarrow x = 1.33 \times 10^{-3} = [OH^-]$

So $[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.33 \times 10^{-3}} = 7.51 \times 10^{-12}$

$pH = -\log(7.51 \times 10^{-12}) = 11.12.$

On addn of 25 mL of 0.1M HCl solⁿ.

$\therefore$ mmoles of HCl $= 0.1 \times 25_{mL} \Rightarrow$ 2.5 m mol of HCl.

In 50.0 mL of 0.10 M HCl $\Rightarrow$ $50 \times 0.10M =$ 5.0 mmoles of NH_3 solⁿ.

After neutralization mmoles of NH_3 left = 2.5 mmoles.

Total volume of solⁿ = 50mL + 25 mL = 75 mL.

$\therefore$ the resulting solⁿ conc $= \frac{2.5 \text{ mmoles}}{75 \text{ mL}} \Rightarrow 0.033M$

So Now, $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

at eqlbm $0.033M - y \quad y \quad y$

The final sol^N already has 2.5 m mol NH_4^+ i.e 0.033M

∴ total conc of $[NH_4]^+ = 0.033 + y$

as y is small, ∴ $[NH_4OH] \simeq 0.033M$ and $[NH_4^+] = 0.033M$

so $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{y\,(0.033)}{(0.033)} = 1.77 \times 10^{-5}$

$[OH^-] = 1.77 \times 10^{-5} M$.

$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.77 \times 10^{-5} M} = 0.56 \times 10^{-9}$.

$\boxed{pH = 9.24.}$

Buffer Solutions :-

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called buffer solutions.

many body fluids needs definite pH, it is also required in chemical and biochemical processes.
Many medical and cosmetic formulations require that are to be kept and administered at a particular pH.

Buffer capacity:- The capacity of a solution to resist alteration in its pH.

Buffer Index :-(β)

$$\beta = \frac{dB}{d(pH)}$$

dB = amount of strong base added to buffer.

$$\beta = \frac{dB}{d(pH)}$$

So it is the amount of alkali required to change the pH of a buffer solution by unity

The quantity dB is given in moles per 100 g of the solvent.

β is always a positive quantity.

Addⁿ of a strong acid is equivalent to negative addⁿ of base, that is dB becomes -dB and dpH becomes -dpH (as pH lies on the addⁿ of the acid) ∴ β is +ve.

Buffer sol'n are considered to posses reserve acidity as well as reserve alkalinity. ∴ NH_4Ac has reserve acidity due to presence of NH_4^+ ions and reserve alkalinity due to presence of CH_3COO^- ions.

MOST OF THE INNPORTANT BUFFER SOLUTIONS USUALLY CONSISTS OF MIXTURE of EITHER WEAK ACIDS AND THEIR SALTS OR WEAK BASES AND THEIR SALTS.

I) Buffer Mixtures of a weak acid and its Salt :-

a common buffer :- equimolar sol^n of Acetic Acid and sodium acetate.

AcH weakly dissociated where as NaH being a strong electrolyte, completely dissociated

So Now suppose a strong acid is added to above mix. H^+ will be taken up by CH_3COO^- to form slightly dissociated CH_3COOH.

∴ In a way the H^+ ions are neutralized by the acetate ions present in the mixture. There is a very little change in the pH of the mixture.

$$H^+ + CH_3COO^- \longrightarrow CH_3COOH$$

feebly dissociated

On the other hand if OH^- ions are added

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

again only a small change in the pH.

II. Buffer Mixture of a Weak Base and its Salt

Equimolar sol" of NH_4OH and NH_4Cl

This mixture has undissociated NH_4OH and NH_4^+ and Cl^-

If a strong acid is added

$$H^+ + NH_4OH \longrightarrow NH_4^+ + H_2O$$

If strong base is added

$$OH^- + NH_4^+ \longrightarrow NH_4OH$$

So here reserve acidity is due to NH_4^+ and reserve alkalinity is due to NH_4OH.

Calcutta